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DOCUMENT-IDENTIFIER: US 5871680 A
TITLE: Method and apparatus for spinning hollow fiber membranes

Abstract Text (1):
A process for the preparation of anisotropic hollow fibers useful as permselective separation membranes and for producing composite membranes thereof, involves extruding a spinning dope through a spinneret that extends into a coagulation chamber maintained at subatmospheric pressure, conveying the nascent hollow fiber through a column that extends into the reduced pressure chamber, and contains at least two different abutting liquids arranged in sequence. An apparatus for conducting the process includes the vacuum chamber, the spinneret and the column that extends into the vacuum chamber and is equipped with entrance and exit ports for introduction and removal of at least two abutting liquid coagulation media.

Brief Summary Text (4):
There are numerous examples in the literature of processes that describe the preparation of fluid separation hollow fiber membranes. These membranes can be either anisotropic, most frequently asymmetric, or isotropic, and may be useful for a variety of fluid separations, including gas separations. For example, I. Cabasso describes the procedures for preparing porous polysulfone hollow fibers in "Hollow Fiber Membranes", Kirk Othmer: Encyclopedia of Chemical Technology, 12, 3rd Edition, 492-519 (1980) and "Membranes", Encyclopedia of Polymer Science and Engineering, 9, 2nd Edition, 509-579, (1987).

Brief Summary Text (7):
A procedure for preparing fibers from polymer solutions at subatmospheric pressure is disclosed by Stoy et al. in U.S. Pat. No. 3,842,151. According to the invention disclosed, a polymer solution is extruded through a spinneret into a tube or shaft whose upper end is sealed against gas flow by a lid connected with the spinneret, and its lower end is placed below the level of a coagulation bath open to the atmosphere. The pressure within the tube between the spinneret and the level of the coagulation bath is maintained lower than the pressure outside the tube or shaft which causes the level of the coagulation liquid to be higher in the shaft than in the outer coagulation bath. In the spinning process, the polymer solution is extruded through the spinneret into the gaseous atmosphere above the coagulation bath in the shaft, which is maintained at subatmospheric pressure. The fibers then enter the coagulation bath and after passing through the bath are collected. Vacuum means are provided to maintain the level of the coagulation bath at the desired height and provision is also made to introduce and remove gaseous medium from the shaft area between the spinneret and the top of the coagulation bath if desired.

Brief Summary Text (9):
B. Bikson et al. in U.S. Pat. No. 5,181,940 describe the use of a vacuum spinning apparatus to produce highly asymmetric hollow fiber membranes with improved fluid or gas separation properties. The spinning dope is extruded into a zone maintained at a reduced pressure as compared to the exterior of the spinning chamber and the cast dope is subjected to controlled evaporation under the subatmospheric pressure prior to being introduced into the homogeneous liquid which acts as the coagulation medium.

Brief Summary Text (11):
This invention relates to the manufacture of improved hollow fiber fluid separation

membranes, to a process for producing anisotropic hollow fiber membranes for fluid separation and to the apparatus used to conduct the membrane production process. More particularly, the invention relates to a process for spinning hollow fibers in an apparatus equipped with a vacuum chamber and then precipitating the nascent hollow fiber and leaching out solvent (frequently including leaching non-solvent pore forming agents and other additives as well) by passing the nascent fiber through a plurality of quench liquids of different compositions without intermittent exposure to the surrounding atmosphere. As a result, it is possible to produce hollow fiber membranes with improved fluid or gas separation properties. The invention also more particularly relates to an apparatus which includes a spinneret extending into a vacuum chamber and a column which contains multiple abutting coagulation liquids also extending into the same vacuum chamber.

Detailed Description Text (2):
The process for preparing anisotropic, in particular "skinned" or asymmetric membranes, by phase inversion process in accordance with the present invention involves two steps, i.e. the spinning of a polymer solution or dope and the passage of the spun fiber membrane through a plurality of abutting coagulation media. It will be appreciated that a number of events occur when the nascent fiber is subjected to the coagulation media including solidification/precipitation as the result of the phase inversion process, leaching out the solvent components of the solution, and in some cases leaching out any non-solvents, pore forming agents and other additives. The process can also include a number of optional steps such as annealing of the spun hollow fiber membrane and/or a controlled evaporation from the nascent membrane before exposure to the coagulation media. The fibers can be produced following the teachings of this invention by a dry-wet spinning process or by a wet-wet spinning process. In the latter instance, the properties of the resulting membrane are primarily controlled by the coagulation media. In the former instance, the properties are affected by the evaporation step.

Detailed Description Text (3):
In producing anisotropic porous hollow fibers by this invention a solution of the fiber-forming material is prepared, said solution commonly being referred to as a sol, a spinning dope or a spinning solution. The dope contains the fiber forming material, typically a polymer (or mixtures of polymers) mixed with a vehicle comprised of one or more components to yield a mixture having a viscosity suitable for the spinning of hollow fibers. The vehicle with which the polymer is mixed usually has at least one solvent capable of dissolving the polymer along with one or more additives that may be nonsolvents, as is well known in the art. The hollow fibers are prepared by spinning polymeric solutions or dopes that are close to the point of incipient gelation or gels through a zone of reduced partial pressure followed by solidification in coagulation media. Advantageously, the dope is prepared by dissolving one or more polymers in a solvent system containing at least one additive such as a nonsolvent, a pore-forming agent, or surfactant.

Detailed Description Text (4):
The spinning solution may contain solvent or nonsolvent components of high vapor pressure to promote solvent evaporation in the reduced pressure gap during the dry-wet spinning process. In some instances, it may be beneficial to have a mixture of high boiling and low boiling solvents as a part of the spinning solution. However, it is not required to incorporate low temperature boiling solvents into the spinning solution to attain high levels of fiber asymmetry, and solutions comprised of high boiling solvents only can be utilized effectively.

Detailed Description Text (7):
The nonsolvent components used in formulating the dope can be solids or liquids. These components are useful in controlling the viscosity of the spinning dope as well as the porosity and other properties of hollow fibers prepared. Typical liquid nonsolvents known to be useful in formulating spin dopes are aliphatic alcohols, particularly polyhydric alcohols, such as ethylene glycol, glycerine, etc., polyethylene oxides and polypropylene oxides, surfactants such as alkylaryl polyether alcohols, alkylaryl sulfonates, alkyl sulfates, etc., triethylphosphate, formamide, aliphatic acids such as acetic or propionic acid, etc. Examples of solid material nonsolvents include polyvinylpyrrolidone, citric acid, and salts, such as zinc chloride, lithium chloride, etc.

Detailed Description Text (8):
The spinning dope should have a viscosity high enough to provide adequate strength to the hollow fiber precursor as it is extruded from the spinneret. The viscosity of the dope at the extrusion temperature should be about 1,000 to 10,000,000 centipoise, preferably about 10,000 to 1,000,000 centipoise.

Detailed Description Text (9):
The spinning dope can be prepared by first adding the solvent components of the vehicle to a suitable mixing vessel and subsequently adding the nonsolvent components and stirring until a homogeneous mixture is obtained. The fiber-forming polymer may then be added to this vehicle and mixed for a sufficient time to completely dissolve the polymer. It is advantageous to use a mechanical stirring device capable of mixing the resulting viscous mixture. Mixing of representative spinning dopes may be accomplished in less than 24 hours, often in about 8 hours.

Detailed Description Text (10):
Following the completion of the mixing process, the spinning dope must be deaerated; that is, any bubbles that have been entrained in the dope during the mixing cycle must be removed prior to spinning the dope into hollow fibers. This step is taken so that large defects in the porous hollow fiber are not formed by air bubbles causing disturbances in the hollow fiber extrusion process. Deaeration may be accomplished by subjecting the spinning dope to a vacuum in a suitable vessel or by other methods well known in the art.

Detailed Description Text (11):
Prior to being delivered to the spinneret, it is beneficial for the dope to undergo one or more filtration steps. It is desirable to remove any contaminants from the spinning dope in order to prevent flow disruptions at the spinneret, as well as to prevent large defects in the porous hollow fiber that may lead to poor mechanical properties or decreased separation efficiency. Filters with a nominal pore size rating of about 100 microns are useful for this process, although filters with nominal pore size ratings down to 20 microns or 10 microns may be preferred in some instances.

Detailed Description Text (14):
The spinning dope can be delivered to the spinneret from a supply source by any means known in the art that will provide a consistent flow at the desired rate. Representative of methods used for spinning dope delivery is to force the material from a supply vessel to the spinneret under gas pressure while metering the flow with a suitable regulating valve and rotameter assembly. Alternatively, a pump may be employed to meter the dope to the spinneret. Another method would be to employ a combination of pressure vessels and pumps to accomplish this task. Typical flow rates for dope delivered to the spinneret in practicing this invention are in the range of 0.5 cc/minute to 20 cc/minute, preferably from 1 cc/minute to 10 cc/minute. However, this is dependent upon the size of the spinneret and number and size of the orifices.

Detailed Description Text (16):
It may often be advantageous to heat the spinning dope prior to extrusion from the spinneret. This may be useful sometimes from the point of view of reducing the viscosity of the spinning dope to make it easier to handle. In addition, asymmetric porous hollow fiber with more beneficial properties may in some instances be obtained by delivering the spinning dope at elevated temperatures. Dope temperatures at the spinneret are frequently in the range of from about 20.degree. C. to 200.degree. C., preferably from about 30.degree. C. to 150.degree. C.

Detailed Description Text (17):
In order to maintain an open bore in the extruded spinning dope stream, a core fluid is delivered through the tube in the spinneret. This core fluid may be liquid or gaseous and may consist of a single component or a mixture of components. The core fluid is delivered to the spinneret tube at a rate that will yield a fiber of the desired size. The flow rate of liquid bore fluids metered to the spinneret may be measured by means of any known suitable device, such as a flowmeter. These bore fluids may be delivered to the spinneret by means of a metering pump or

alternatively, by forcing the liquid from a vessel by means of gas pressure. Gaseous bore fluids may be delivered by using a metered compressed gas. Alternatively when using the dry-wet process, one can take advantage of the pressure differential between the bore of the spinneret tube and subatmospheric pressure within the chamber that encases the spinneret to aspirate the core fluid into the spinneret.

Detailed Description Text (20):
FIG. 1 shows a multiple coagulant spinning apparatus adapted to produce hollow fibers by dry-wet spinning process. The apparatus includes vacuum chamber 1 that is connected through port 2 to a device that establishes a vacuum within chamber 1, such as a vacuum pump (not shown). Extending vertically into the vacuum chamber 1 from the top is spinneret 3. Spinneret 3 may be positioned partly or completely within the vacuum chamber 1. The vacuum chamber 1 is optionally further equipped with inlet and outlet ports 4 and 5 that can be utilized for intermittent or continuous circulation of gases or vapors such as, for example, inert purge gas. An example of such a gas circulation system is described by Stoy et al. in U.S. Pat. No. 3,842,151, incorporated herein by reference.

Detailed Description Text (21):
In the dry-wet spinning process of this invention, the dope and the core fluid are extruded from the spinneret 3 to form nascent hollow fiber 20, the spin dope and core fluid delivery systems are not shown. The nascent hollow fiber is transported through gap 6 that is formed by positioning the spinneret 3 at a predetermined distance above the upper end of column 7 containing the coagulation liquids. The upper end of column 7 is sealed in the vacuum chamber 1 and the lower end is placed below the level of the coagulation bath in the reservoir 17 that is open to the atmosphere. The nascent hollow fiber is exposed to gaseous atmosphere at reduced pressure in the vacuum chamber 1 for a predetermined period of time prior to contact with coagulation liquids. The exposure of the hollow fiber stream to subatmospheric pressure in the gaseous gap 6 can result in improved hollow fiber properties as compared to fibers spun at otherwise similar conditions but at an atmospheric pressure. The length of gap 6 can be from about 0.25 cm or less to about two meters or more, but generally is from about 0.5 cm to about 30 cm. The vacuum level in the chamber will vary from about 1 cm to about 75 cm Hg, and is frequently from about 10 cm Hg to about 36 cm Hg. The vacuum should not be maintained too high so as to cause rupture of the hollow fibers as they pass through the vacuum chamber or lead to an undue evaporation of the coagulation fluid.

Detailed Description Text (22):
Column 7 is a hollow elongated tube having an internal diameter generally of about 1 to 30 cm and a length of generally about 25 to 900 cm. Column 7 contains two abutting coagulant liquids arranged in series in zones 8 and 9. Depending on the miscibility of the abutting liquids, there may be some intermixing at the interface between the two zones. For convenience, the first coagulant with which the nascent hollow fiber comes into contact will hereafter be designated as the primary coagulant. One of the advantages of the present invention is that it permits the use of primary coagulant that is toxic or flammable in nature. Because the head space in the vacuum chamber 1 is enclosed and maintained at reduced pressure, most of the oxygen can be easily removed by purging chamber 1 with an inert gas prior to introduction of the coagulant liquids into the column 7 and/or continuously throughout the spinning process. The oxygen deficient atmosphere in vacuum chamber 1 will not support combustion and thereby provides a means to work safely with flammable coagulation liquids. Another advantage of the invention is that the volume of the primary coagulation liquid may constitute only a small percentage of the total coagulant volume in the column, thereby providing an economical means of utilizing expensive primary coagulation liquids.

Detailed Description Text (26):
The primary and the secondary coagulants serve to solidify the extrudate. Solvent-nonsolvent interchange takes place during the coagulation process culminating in phase inversion with the polymer-rich phase forming the solid regions and the polymer-lean phase forming the pores. In certain spinning formulations, the phase inversion process will take place only upon contact with the secondary coagulation liquid, while in other spinning formulations the secondary liquid is used for washing purposes only. Each of the coagulants or quench liquids can contain

one or more components that are miscible with the solvent components of the spinning dope, and each of the coagulation liquids can be a single liquid and/or a mixture of several components that will conveniently coagulate or precipitate the dope. Typical examples of coagulation liquids are water, alcohols and their mixtures with water, aqueous salt solutions and the like. The residence/contact time in each of the coagulation baths should be long enough to permit the desired degree of diffusion of solvent components out of the fiber and sufficient diffusion of coagulant into the fiber so that an integral structure is achieved in the fiber prior to exiting the secondary coagulation liquid and being collected/transported by a take-up equipment (not shown) or other suitable collection means.

Detailed Description Text (27):
The coagulants can be optimized to obtain desired hollow fiber membrane characteristics. For instance, when making asymmetric gas separation membranes, it may be desirable to use a primary coagulant with strong nonsolvent characteristics that will quickly set up the nascent filament and promote efficient removal of the spinning dope solvents. This strong coagulant can lead to a thin nonporous membrane skin or surface layer. Conversely, it may be more desirable to have a primary coagulant that is enriched with a solvent component for the membrane forming polymer when spinning high surface porosity microfiltration or ultrafiltration membranes. Membranes of this type often require large pores and highly porous surfaces that can be formed during a slower coagulation process.

Detailed Description Text (30):
The composition of the primary coagulation fluid at the top of the column will differ from the composition of the secondary fluid at the lower portion of the spinning column. There should be a difference of at least 1%, and preferably 5% or more, in the concentration of at least one component of the coagulation fluids injected into the different coagulation zones of the apparatus used in the process of this invention. This concentration difference would be the minimum to define a separate coagulation fluid.

Detailed Description Text (41):
FIG. 2 illustrates another embodiment of the present invention in which more than two coagulation liquids are employed and also illustrates the adaptation of the apparatus to a wet/wet spinning process. In FIG. 2, the same numerals have been used to illustrate the parts and features that are common with those of the apparatus shown in FIG. 1. In the FIG. 2 embodiment, the gap 6 between the spinneret and the first coagulation liquid has been eliminated, and the spinneret 3 extends below the liquid level in column 7 so that the nascent fiber membrane contacts the primary coagulant immediately upon leaving the spinneret 3. The vacuum chamber 1 does not have to be evacuated continuously during the spinning process. Typically the vacuum is generated through the exit port 2 during start up of the spinning process to fill the column 7 with coagulation liquids. Column 7, as illustrated in FIG. 2, contains three coagulants, the primary coagulant in the uppermost zone 8 followed by coagulants in zones 9 and 10. The coagulation liquids are introduced through ports 11, 12 and 13 and withdrawn through ports 14, 15 and 16 as shown. To prevent excessive intermixing it is desirably to place the lowest density coagulation liquid at the top of the column in zone 8 and the highest density liquid into the bottom zone 10 and container 17. Upon exiting spinneret 3, the nascent hollow fiber 20 follows the path indicated by the arrowed line. The hollow fiber contacts sequentially abutting coagulants in zones 8, 9 and 10, traverses guide roll 21 or a similar body, and then is transported to the take up or washing equipment. In some embodiments, the primary and the secondary coagulants can be highly miscible, which may make it difficult to maintain a distinct interface between the zones. To minimize intermixing, a third liquid that exhibits limited solubility in coagulant liquids in zones 8 and 10 can be placed in the intermediate zone 9 so as to maintain a distinct interface with the primary and secondary coagulants in zones 8 and 10. Furthermore, it is also possible to employ a liquid in zone 9 that is substantially inert and does not effect coagulation, but serves to separate miscible primary and secondary coagulants in zones 8 and 10.

Detailed Description Text (48):
A spinning dope was prepared by mixing 38.5 parts of polysulfone, Udel.TM. 3500, 6 parts of maleic anhydride, and 55.5 parts of dimethylformamide to form a homogeneous

solution. The solution was deaerated and spun into hollow filaments in the apparatus shown in FIG. 1. To form a nascent hollow fiber, the spinning dope was extruded from a tube-in-orifice spinnerette encased in a vacuum chamber at a rate of 3.4 cc per minute and at the temperature of 71.degree. C. while air was metered into the injection tube of the spinnerette.

Detailed Description Text (51):
A hollow fiber membrane was spun from the same spin dope composition described in Example 1. The spinning, processing and coating conditions were identical to that described in Example 1, except that the hollow fiber was spun into a single coagulation fluid comprised essentially of water. Coated hollow fibers were prepared and tested for air separation properties as described in Example 1. The results are summarized in Table 1 below.

Detailed Description Text (54):
A spinning dope was prepared by mixing 38.5 parts of a polyetherimide resin (Ultem 1000.RTM., General Electric Co.), 15.0 parts of a nonionic surfactant (Triton X100.RTM.), and 46.5 parts of N-methylpyrrolidone until a homogeneous solution was obtained. The solution was deaerated and spun into hollow fiber filaments in the apparatus shown in FIG. 1. To produce the nascent hollow fiber, the spinning dope, preheated to 71.degree. C., was extruded at the rate of 3.0 cc/minute through a tube-in-orifice spinnerette encased in a vacuum chamber, while gamma-butyrolactone was metered into the injection tube of the spinnerette at a rate of 1.2 cc/minute. A level of vacuum in the vacuum chamber was maintained at about 14 cmHg.

Detailed Description Text (57):
A hollow fiber membrane was spun utilizing an identical spinning dope to the one used in Example 2. The spinning, processing, and coating conditions were identical to those described in Example 2, except that the fiber was spun without the benefit of the dual coagulation processes of the present invention. This hollow fiber was coagulated in a 0.05% solution of Triton X100 in water.

Detailed Description Text (60):
Hollow fiber membrane was spun, processed, and coated in a manner identical with that described in Example 2 above, except that the extrusion temperature of the spinning dope was maintained at 82.degree. C. Coated fibers from this experiment were fabricated into modules and tested according to the procedures described in Example 1. The results of the air separation test are summarized in Table 2 below.

Detailed Description Text (62):
Coated hollow fiber membranes were prepared under conditions identical to those in Comparative Example 2 above, except that the extrusion temperature of the spinning dope was maintained at 82.degree. C. as in Example 3 above. Coated fibers from this run were fabricated into modules and tested according to the method described in Example 1. The results of the air separation test are summarized in Table 2 below.

Other Reference Publication (2):
Influence of guench medium on the structures and gas permeation properties of polysulfone membranes made by wet an dry/wet phase inversion, Pinnau.

Other Reference Publication (3):
Journal of Membrane Science, 71 (1992) 81-96; Pore size control technique in the spinning of polysulfone hollow fiber ultrafiltration membranes, Doi, Desalination, 80 (1991), 167-180.